

Progress Report for the Oak Ridge Integrated Field Challenge Implementation Plan

Project ERKP686 “Multi-scale Investigations on the Rates and Mechanisms of Targeted Immobilization and Natural Attenuation of Metal, Radionuclide and Co-Contaminants in the Subsurface”

January - October 2007

In January 2007 the Department of Energy’s (DOE’s) Environmental Remediation Sciences Division (ERSD) awarded the Oak Ridge National Laboratory’s (ORNL) Environmental Sciences Division (ESD) with an Integrated Field Challenge (IFC) project that is located on the Oak Ridge (OR) Reservation in eastern Tennessee. The project encompasses an integrated multi-disciplinary, multi-institutional research program that seeks to provide an improved scientific understanding and predictive capability of subsurface contaminant fate and transport at scales ranging from the molecular to the watershed. The influence of coupled processes on U, Tc, and contaminant NO₃ fate and transport are being quantified along numerous contaminant pathways using subsurface manipulations and the assessment of natural attenuation processes throughout the watershed. These investigations are being integrated with multi-scale numerical studies to provide an accurate predictive capability for long-term site performance and to determine if targeted manipulations are required.

An Implementation Plan was provided to ERSD early in 2007 and it describes a framework of processes and requirements that the project team will follow to safely and efficiently complete the research tasks described in the project proposal. The following is a Progress Report on the 2007 ORIFC Implementation Plan. It discusses (1) management and operational milestones, (2) research accomplishments and products milestones, and (3) responses to reviewer comments on original proposal and potential changes to research focus.

Management and Operational Milestones

The OR Field Research Center Management Plan tiers from the Office of Science Strategic Plan (DOE 2004b), ERSP Strategic Plan (DOE 2006) and ERSD Management Plan for the Integrated Field Challenge (IFC) Projects (DOE 2007) and is one of a set of high-level planning documents (available at <http://public.ornl.gov/nabirfrc/>) that govern the operation of the ORFRC and implementation of the IFC and other projects. These include the following plans:

- Environmental Assessment and FONSI (DOE 2000 a,b)
- Quality Assurance Plan (Brandt et al., 2001; revised 2004; revised 2007)
- Site Characterization Plan and Addendum (Watson et al., 2001; Watson and Roh 2004)
- Health and Safety Plan (Watson and Quarles, 2001; revised 2007) (tiered from the ORNL HAZWOPER Program Manual, 1993)
- Research Safety Summary (ORNL, 2007)
- ORIFC Researcher’s Guide (ORNL, 2005 revised)
- ORFRC Closure Plan (Bogle and Watson, 2006)
- Implementation Plan for the Integrated Field-Scale Challenge Project (ORNL, 2007)

Each Plan is a living document and are constantly revised, reviewed, and reimplemented as new research are initiated at the ORFRC.

Regulatory Compliance: The regulatory framework for operating the ORFRC and implementing new projects at the site has been agreed upon with the regulators through a modification of the Bear Creek Hydrogeologic Regime RCRA Post Closure Permit.

Preparation of detailed IFC Task Plans: In addition to the existing higher level operational plans, detailed IFC project task plans have been prepared describing each work phase that is currently, or will be conducted at the ORFRC.

Health and Safety: Specific Environment, Safety, Health, and Quality (ESH&Q) requirements for activities conducted at the ORFRC are determined on a project-by-project basis through individual Integrated Safety Management System (ISMS) project reviews conducted in accordance with, and as described in, the ORFRC Management Plan. The ORNL Environmental Sciences Division has a rigorous, web-based Research Safety Summary documentation that keeps projects in compliance with all aspects of the Law.

Data Management: The Quality Assurance Plan has been updated to include data management and quality control procedures that are being implemented for the IFC project.

Collection and Shipping of Samples to Researchers: Groundwater and sediment samples have been provided to ERSD researchers upon request provided they have the appropriate radionuclide licenses in place to accept the samples. David Watson has been working closely with various ERSD projects (e.g. Barkay, Sobecky, Palumbo, Kostka), not funded by the ORIFC, with regards to sample requests, borehole installations, and other needs. Thus far, sediment and groundwater samples have gone to: Sobecky (U. Georgia), Kostka (FSU), Palumbo (ORNL), Zhou (OU), Hazen (LBNL), Barkay (Rutgers), Bank (U. Buffalo), and Fields (Montana State).

Waste Management and Site Closure Activities: Waste disposal procedures are described in the Management Plan and, except for the cost of characterizing the wastes, there is no cost to the project for disposing of ORFRC wastes. Site closure activities are documented in the 2006 Closure Plan.

Reporting and Review: The PI and Field Site Manager have participated in quarterly conference calls with the ERSD Program Manager. In addition, they have provided written quarterly reports (4 reports, of which this is one) of operational and research activities and have provided these to the ERSD Program Manager, Paul Bayer.

In addition, (1) a regulatory framework for operating the ORIFC and implementing new projects at the site has been agreed upon with the regulators through a modification of the Bear Creek Hydrogeologic Regime RCRA Post Closure Permit; (2) detailed ORIFC project task plans have been prepared by each research scientist describing the various work activities and scheduled that are currently being conducted, or will be conducted by the ORIFC; (3) a Local ORIFC Review Panel (LORP) that includes local representatives from DOE ORR Environmental Management, the cleanup contractor (BJC), and State regulators has been formed to provide the Field Site Manager and IFC Principal Investigator with input on day-to-day operational issues, project relevance to site needs, regulatory compliance issues, and an avenue to communicate the results of research studies to some of the local stakeholders; and (4) detailed ORIFC quarterly progress reports and conference calls on operational and research activities have been provided to ERSD program managers.

Funding Scenario

Capital funds have been requested through the ERSD for the purchase of a new drill rig for the ORFRC which would replace our currently aging and deficient drill rig.

All subcontracts and inter-laboratory fund transfers are complete. The various institutions receiving funds from the ORIFC are:

- FPM Geophysical & UXO Services for geophysics
- Battelle for geophysics
- BWXT Engineering for penetration permits
- BWXT Lab services

- BJC site and regulatory support
- Univ Oklahoma (Zhou)
- Stanford University (Criddle)
- Georgia Tech (Luo)
- Florida State University (Kostka)
- University of Tennessee (Baker)
- Argonne National Laboratory (Kemner)
- Lawrence Berkeley National Laboratory (Hubbard)

Research Accomplishments and Products Milestones

The scientific and technical advances that the ORIFC has delivered during the first year effort have been extraordinary as exemplified by our research findings and our publication and presentation listings. Examples of significant research endeavors include; (1) several highly successful field scale experiments that coupled hydrology, geochemistry, microbiology, and numerical modeling to quantify the adverse impact of groundwater nitrate and dissolved oxygen intrusion on subsurface U(IV) reoxidation and mobilization in bioreduced zones, (2) extensive experimental and numerical research involving pH manipulation studies designed to immobilize U and Tc in situ, and to create subsurface conditions conducive to biological denitrification, (3) initiation of novel watershed scale datasets that cross-correlate surface geophysical electrical resistivity measurements with observed groundwater geochemistry thus allowing for large scale spatial and temporal monitoring of contaminant plume dynamic and an enhanced understanding natural attenuation and recharge processes at the site, (4) the identification of unique U-rich minerals in field sediments using a variety of high-resolution interfacial spectroscopy techniques, and (5) application of isotopic methods for quantifying large scale contaminant fate and transport mechanisms that control natural attenuation processes. Besides our immediate project tasks, extensive groundwater and sediment samples have been provided to nearly a dozen ERSD researchers that have research goals relevant to the ORIFC. The ORIFC has also produced more than 30 published or submitted peer-reviewed journal articles this year and nearly as many presentations at national and international scientific meetings. The project PI and Field Research Manager have been active participants in the DOE Oak Ridge Reservation Closure Project Team in order to ensure remediation planning needs are addressed and technical insights are transferred into DOE remediation efforts. In summary, this project is on schedule to deliver multi-scale predictive monitoring and modeling tools that can be used at sites throughout the DOE complex to inform and improve the technical basis for decision making, and to assess which sites are amenable to natural attenuation and which would benefit from source zone remedial intervention.

General Achievements

David Watson was an invited speaker to the Oak Ridge Site Specific Advisory Board (SSAB) on the new ERSD ORIFC project - January 17, 2007.

The History Channels Modern Marvels aired a television show on DOE's environmental bioremediation research at the ORIFC where David Watson and Philip Jardine were interviewed – January 24, 2007.

David Watson held a meeting with Elizabeth Phillips from DOE Oak Ridge Operations to discuss project impacts on future Records of Decision concerning OR groundwater remediation - February 23, 2007.

Several press releases were issued in January 2007 from ORNL and collaborators Florida State University and the University of Tennessee.

Local IFC review committee has been formed through formal invitations to participate. Committed members included: Elizabeth Phillips (DOE EM), Dick Ketelle (BJC- EM contractor) and Robert Benfield (State regulator).

The IFC project team attended the ERSP annual meeting held April 15-19 at the National Conference Center Lansdowne Virginia. The project team (Phil Jardine, Dave Watson, Craig Criddle, Susan Hubbard, Joel Kostka, and Jack Parker) gave a comprehensive 2 hour long overview of the Oak Ridge IFC project to the DOE, other ERSP PIs and the FREC. The IFC project team held a project kickoff meeting on Sunday the 15th and held several breakout sessions during the ERSP meeting to plan and coordinate various components of the project.

DOE-Environmental Management has commissioned the National Academy of Science to study and report on the state of R&D (both short term and long term- 10 to 20 years). ORNL hosted a NAS visit on June 13 and 14 where Philip Jardine and David Watson provided a presentation and field tour related to previous and current research endeavors at the Oak Ridge Field Research Center.

David Watson provided a tour of the ORFRC to visitors from Penn State who are members of the NSF funded Center for Environmental Kinetics Analysis which is located at Penn State. He discussed current and future research endeavors and discussed opportunities for collaboration.

DOE officials Paul Bayer and Todd Anderson visited ORNL on June 25 and 26 to discuss research activities at the ORFRC and reporting requirements for the ORIFC. They also were provided a tour of the watershed that is to be used by the ORIFC effort. Discussions were also held as to how the ORIFC research was linked to the new SFA proposal on Hg and U(0).

The Interstate Technology Regulatory Council's Bioremediation of Dense Non-Aqueous Phase Liquids (BioDNAPL) Team, selected Oak Ridge as the location of their September 5-6, 2007 meeting. The location was selected so that they could take advantage of the Department of Energy's bioremediation programs, research, and expertise in this field. One of the ITRC goals was to educate and train its members on the latest technologies. In addition they strive to transfer this knowledge to ITRC member states in the form of products, such as case studies and guidance documents. They also wanted to learn that DOE's bioremediation technology information needs so that they can incorporate this knowledge into their future products. The ITRC requested a tour of the ERSD Oak Ridge Field Research Center in order to demonstrate to their members the scientific achievements being discovered there and to meet other staff members working on bioremediation technologies. David Watson and various individuals of the ORIFC team provided the tour on September 6, 2007. The interaction with ITRC members was stimulating and should lead to increasing technology transfer of ORIFC research findings to applied bioremediation strategies around the country.

During this report period (Jan.1 – Sept 30, 2007), numerous manuscripts (~30) have been accepted for publications including (1) Wu et al. (2007) Environ. Sci. Technol. that describes field experiments in Area 3 that investigated the impact of dissolved oxygen on U reoxidation and mobilization, (2) Amos et al. (2007) App. Environ. Microbiol. that describes *Geobacter lovleyi* strain SZ in the Area 3 biotreatment zone, (3) Luo et al. (2007) Appl. Microbiol Biotechnol. that describes changes in microbial communities within biostimulated sediment sample from Area 3, and (4) Phillips et al. (2007), Environ. Sci. Technol., that quantifies geochemical and hydrologic controls on the deposition of U(VI) in ORIFC saprolite. Numerous papers have been published as well, with a list provided below.

Numerous presentations of research and overviews of ORFRC activities were provided to the scientific community. These included presentations at the American Society of Microbiology 107th General Meeting in Toronto, Canada, May 21-25, the U2007 Global Uranium Symposium, Corpus Christi, Texas, May 21-24, 15th Annual International Conference on Microbial Genomics, 16-20 Sept, College Park, MD, the Institute for Geosciences, Friedrich-Schiller University, Jena, Germany, and the 4th Symposium on Biosorption and Bioremediation, held in Prague, Czech Republic, August 26th - 30th, 2007. A list of presentations and abstracts are provided below.

Personnel Achievements

Susan Hubbard has been invited to speak at the 2007 Fall American Geophysical Union National Meetings, December 10–14 in San Francisco CA. Her presentation is entitled “Exploring Hydrological and Biogeochemical Processes associated with Remedial Treatments using Geophysical Methods”. She has also been named a co-editor of the Vadose Zone Journal starting her appointment as of June, 2007 and she has served on the Scientific Advisory Board of the German National Laboratory in Jülich – May 2007. In addition, Susan is an organizer of the Computational Methods in Water Resources Conference, which is scheduled to be held in July 2008 in San Francisco: <http://www-esd.lbl.gov/CMWR08/index.html>.

Gregory Baker will present or has presented invited talks at: (1) “Near Surface 2007” conference of the European Association of Geoscientists & Engineers, Istanbul Turkey, September 2007; (2) Geological Society of America conference in Denver, Colorado, November 2007; (3) International Conference on Environmental and Engineering Geophysics (ICEEG), Wuhan China, June 2008; and (4) will give a 2-day invited short course on “Near Surface Seismic Techniques” for the Society of Exploration Geophysicists, Houston Texas, November 2007.

Gregory Baker was also awarded “Best Paper” for a presentation at the SAGEEP 2007 conference (Symposium on the Application of Geophysics to Engineering and Environmental Problems) in Denver, Colorado, for “Combining Seismic and Ground Penetrating Radar Techniques to Analyze Geologic Controls of Riparian Meadow Complexes in the Central Great Basin, Nevada USA”. In addition, he became (1) an associate editor for the Journal of Geoscience Education in February 2007, (2) a member of an exploratory editorial board for the proposed new Society of Exploration Geophysicists (SEG) journal on applied geophysics (title TBA) July 2007, and (3) an elected official to a three-year term on the Board of Directors of the Environmental and Engineering Geophysical Society, April 2007.

Phil Jardine has been invited to provide the keynote presentation at the Center for Environmental Kinetics Analysis (CEKA) “All Hands” 4th Annual Meeting, Penn State University on October 17, 2007. His presentation is entitled “Exploring Subsurface Contaminant Fate and Transport Processes at Multiple Scales” which will focus on past, current, and future research at the ORIFC site.

Joel Kostka at Florida State University has established a number of international collaborations that will greatly expand the ORIFC project capabilities to address microbiology at the watershed scale.

Research Achievements

Research accomplishments are organized by Task (i.e. A through D) as outlined in the ORIFC proposal or are listed as ‘general’ achievements that pertain to all or multiple tasks.

Task A – Geophysical Definition of Subsurface Heterogeneity within Pathways

Significant progress has been made on all four key geophysical and monitoring tasks which include (1) planning; (2) equipment fabrication and laboratory development; (3) geophysical characterization and error assessment at the field scale, and (4) the development of numerical approaches that are needed to integrate various datasets for quantitative characterization and monitoring purposes. Watershed scale datasets are being established which cross-correlate surface geophysical electrical resistivity and seismic refraction velocity measurements with observed groundwater geochemistry and depth to refusal at the ORIFC. Research is allowing us to track large scale spatial and temporal changes in contaminant plume dynamic as a function of long-term seasonal patterns and short-term storm events.

Research has investigated the frequency, amplitude, and natural variability of geophone response over time using multiple strategies in geophone placement to better define and constrain standard operating procedures for future time-lapse 2D and time-lapse 3D (i.e., 4D) near-surface seismic surveys.

In order to use time-lapse measurements to provide quantitative information about recharge processes, it is imperative that (1) we develop petrophysical relationships between the geophysical and hydrogeochemical properties of interest; (2) we assess the error associated with time-lapse geophysical datasets; and (3) we develop analysis approaches capable of integrating the disparate datasets as needed to explore changes in subsurface geochemistry due to recharge dilution. We have recently initiated studies to tackle these three important components. Both lab and field experimental apparatus have been fabricated to permit development of geophysical-hydrogeochemical petrophysical relationships with an example being the development of an electrode string that has been permanently installed next to the S-3 ponds area where numerous multilevel sampling wells are also located for recharge investigations. Preliminary surface electrical transects have been collected in the S-3 recharge study area and all efforts have been coordinating with the entire project team to plan the drilling and sampling of new boreholes in the same area. The new wellbores will be used to collect hydrogeochemical-geophysical-microbiological datasets, which will in turn be used to start to develop site-specific, field-scale petrophysical relationships. These relationships are needed for use with the geophysical datasets to quantitatively estimate plume distribution and to monitor changes in TDS associated with recharge. This information will serve to provide an enhanced watershed wide understanding and predictive capability of natural attenuation and recharge processes at the site. This subtask directly addresses hypotheses 1 through 3 of the proposed research.

LBNL is working on a refraction inversion code from which a seismic-penetration depth inversion framework will be developed. In conjunction with David Watson, field efforts are underway to determine optimal hole size, placement, and drilling methodologies for cross-hole geophysics research. Geophysics wells are currently being installed in the recharge research area.

Task B – Quantifying Rates and Mechanisms of Natural Attenuation

Batch and column scale pH manipulation experiments have been completed. These involve a well coordinated effort between geochemists, microbiologists, geophysicists, and numerical modelers. The modeling of batch and column data has been rigorous and extensive with two peer-reviewed publications nearly ready for submission (see Zhang et al. below). The column flow experiments are currently being scaled-up in order to determine optimal parameters (e.g. pore water velocities, reactant concentrations, and mass transfer rates) for field scale manipulation experiments. Extensive coordination between geochemistry, geophysics, microbiology, and numerical modeling has become routine during the design and implementation of the experiments. This subtask directly addresses hypothesis 1 of the proposed research.

Continuous water level and temperature monitoring of wells near the S-3 Ponds diversion ditch and proposed pH manipulation plot is being conducted to help assess impacts of rainfall/recharge on groundwater and perched zone groundwater conditions. We also continue to monitor the gas tracer test conducted in this area and dissolved gases in general. This subtask directly addresses hypothesis 2 of the proposed research.

The **first of its kind** watershed scale dataset has been established which cross-correlates surface geophysical electrical resistivity measurements with observed groundwater geochemistry at the ORIFC. This revelation will allow us to track large scale spatial and temporal changes in contaminant plume dynamics as a function of long-term seasonal patterns and short-term storm events. This information will serve to provide an enhanced understanding and predictive capability of natural attenuation and recharge processes at the site.

The isotopic signatures of dissolved gases (H_2 , CO_2 , and CH_4) in groundwater were quantified at a variety of spatial locations at the ORFRC in an effort to quantify the mechanisms of H_2 production at the site. The

contribution of evaporated water from the S-3 ponds appears to be significant and most likely has occurred from standing water in S-3 pond before capping. More importantly, the measured $\delta^2\text{H}$ values of H_2 are perhaps the strongest indication to date for their radiolytic origin. The H_2 bears an isotopic abundance highly unusual for shallow ground or surface water and is consistent with radiolysis and not very consistent with microbial biogenesis. Isotopic (H and O) analyses on groundwater itself collected at the same time as the gases suggests the H_2O isotopic signature deviates significantly from that expected from a meteoric origin particularly for groundwater closest to the S-3 ponds. The interpretation of these initial findings is not straight forward at present, except to say that isotopic abundances in both the groundwater and its dissolved gases are unusual and further study should provide insights into contaminant fate and transport mechanisms at the site. This subtask directly addresses hypothesis 3 of the proposed research.

Task C – Enhanced Contaminant Stability Strategies for Source Control

Three highly successful sets of field scale experiments were conducted in Area 3 that investigated the stability of a subsurface bioreduced zone and impact of dissolved oxygen (DO) and nitrate intrusion on U solution and solid phase reoxidation and mobilization. These experiments involved well coordinated efforts between hydrology, geochemistry, and microbiology. Initial results suggest that nitrate reoxidation of reduced U(IV) is significantly more extensive and sustained relative to intrusion by DO. The reoxidized/mobilized uranium (i.e. U(VI)) can be reduced again by re-delivery of the electron donor ethanol which stimulates metal-reducing microorganisms. U(VI) reduction occurred only after nitrate was consumed to a significant extent. The results indicated that low U levels (< US EPA MCL) can be achieved and maintained in a reduced zone with hydraulic protection as outlined in Wu et al. (2006). Nitrite and ammonia were found as metabolic products after nitrate was introduced into the reduced zone. Hydrological, geochemical, and microbial analyses are currently being performed at ORNL, OU, FSU, and, the Institute of Marine and Coastal Sciences. Visualization and modeling endeavors related to these Area 3 experiments are also being conducted by Georgia Tech. and involve (1) multiprocess simulation of nitrate induced reoxidation of U(IV) and (2) concentration distribution plotting of the experimental data. The modeling is also designed to help with field plot expansion and examination of flow field interferences from multiple plots. This subtask directly addresses hypothesis 5 of the proposed research.

Research has been initiated on the use of Ca-oleate as a slow release electron donor source for subsurface microbial stimulation and bioreduction of U(VI). Research has investigated the rates and mechanisms of the oleate precipitation reaction, the mode of subsurface delivery, and the specific microorganisms that are stimulated and knowledge of what their specific activity is with regard to U(VI) reduction. This subtask directly addresses hypothesis 5 of the proposed research.

Task D – Multiscale and Multiprocess Numerical Modeling and Data Analysis

Numerical modeling investigations have resulted in the development of (1) an ion exchange model for the sorption of nickel, uranium and technetium onto amorphous aluminum hydroxide during pH titration of contaminated groundwater utilizing both Na hydroxide and carbonate as titrants (as observed by Gu et al., 2003), and (2) a practical geochemical modeling approach to predict aqueous and solid phase concentrations of various species during titration of aquifer material *in situ* (i.e., aquifer solids and groundwater).

Titration of Area 3 groundwater and subsequent re-injection is being investigated to evaluate metal mobility in response to pH manipulation. A model for geochemical processes governing changes in solution composition during titration of groundwater was developed and tested using the reactive transport code HydroGeoChem (HGC5) (Yeh et al., 2004). The program was used to calculate the isothermal equilibrium distribution of elements between aqueous and solid phases basing on the thermodynamic data for Al (Stumm and Morgan, 1981), Fe (Langmuir, 1997), U (Grenthe et al. 1992) and other relevant elements, together with additional precipitation and sorption/desorption reactions. In order to develop the ion exchange reaction network, the geochemical model HGC5 was coupled with nonlinear parameter estimation code PEST (Doherty, 2002) to

estimate reaction parameters by calibration of corresponding data sets. The concentration profiles of major cations, radionuclides, and SO_4^{2-} during titration of groundwater with NaOH were described well by the model. Solution pH was largely buffered by the hydrolysis of Al resulting in the formation of aqueous hydrolysis species as well as the solid-phase precipitates. Consumption of aqueous U and Tc was modeled by ion exchange reactions representing their sorption onto surface of Al hydroxide. This subtask directly addresses hypothesis 1 of the proposed research.

The soil solid phase was then treated as a polyprotic acid model with a geochemical reaction network that included aluminum and carbonate precipitation/dissolution reactions, ion exchange reactions, and solution complexation reactions. This approach proved to be a practical and accurate means of simulating the soil titration behavior, as well as the distributions of various metal species between aqueous and solid phases.

General

Detection of metabolically-active microbial groups using fluorescence in situ hybridization techniques (FISH) has been underway. This approach lends itself to the enumeration of specific metabolically active microbial populations in low biomass subsurface environments and yet it has not been deployed extensively in the contaminated terrestrial subsurface. Researchers within the ORIFC have developed new probes for the enumeration of metabolically active metal-reducing bacteria in collaboration with international experts in this field. These investigators are also developing techniques to provide direct quantification of the rates and pathways of nitrogen removal from the ORIFC groundwater using membrane inlet mass spectrometry (MIMS) and nitrogen isotope pairing. This technique will partition out the pathways of nitrate removal (denitrification, dissimilatory nitrate reduction to ammonium, anammox) using a state-of-the-art mass spectrometry approach and thus provides the first-ever opportunity to determine whether anammox is a significant pathway of nitrate removal.

We continue to develop new primers and probes for metal- and sulfate-reducing bacteria in ORFRC subsurface materials. We are planning a series of microcosm experiments to test and calibrate our quantitative PCR/message analysis methods to be deployed in ORFRC materials as part of the field project.

We have determined the speciation of uranium in depth profiles of sediments before and after *in situ* biostimulation at the Area 3 site. Previously we found uranyl-carbonates and uranyl-phosphate species in sediments from Area 3 before biostimulation. Recently, we have identified beta-uranyl-oxide as an important solid phase U species and this is the first time this U solid phase has been found in nature. The presence of a beta-uranyl-oxide mineral phase at the ORIFC site is most likely due to the unusual groundwater conditions found near the source (highly buffered, low pH groundwater). These results are significant as remedial success via *in situ* immobilization of U is strongly dependent on the speciation of this contaminant. Solid phase samples acquired after biostimulation at Area 3, were found to have monomeric U(IV) solid phase species that were bound to Fe-oxide coatings. We have also used x-ray microspectroscopy investigation of gravel transects from Area 4 of the ORFRC to identify uranyl carbonate precipitates within the dolomitic gravel zone that were potentially Liebigite and/or Grimselite. Results suggested that uranyl carbonate precipitates containing additional cations were forming on the dolomitic gravel. This subtask directly addresses hypothesis 1 and 3 of the proposed research.

Peer-reviewed publications

Nyman, J.L., H.I. Wu, M.E. Gentile, P.K. Kitanidis, and C.S. Criddle. 2007. Inhibition of a U(VI)- and sulfate-reducing consortia by U(VI). Environ. Sci. Technol. 41:6528-6533.

- Gentile M.E., C.M. Jessup CM, J.L. Nyman, and C.S. Criddle. 2007. Correlation of functional instability and community dynamics in denitrifying dispersed-growth reactors. *Applied and Environmental Microbiology* 73 (3): 680-690.
- Zhang, F., G.T. Yeh, J.C. Parker, S.C. Brooks, M.N. Pace, Y.-J. Kim, P.M. Jardine and D.B. Watson. 2007. A reaction-based paradigm to model reactive chemical transport in groundwater with general kinetic and equilibrium reactions. *J. Contam. Hydrol.* 92:10-32.
- Wu, W., J. Carley, J. Luo, M. A. Ginder-Vogel, E. Cardenas, M. B. Leigh, C. Hwang, S. D. Kelly, C. Ruan, L. Wu, J. Van Nostrand, T. Gentry, K. Lowe, T. Mehlhorn, S. Carroll, W. Luo, W. Fields, B. Gu, D. Watson, K. M. Kemner, T. Marsh, J. Tiedje, J. Zhou, S. Fendorf, P.K. Kitanidis, P. M. Jardine, and C. S. Criddle. 2007. In-situ bioreduction of uranium (VI) to submicromolar levels and reoxidation by dissolved oxygen. *Environ. Sci. Technol.*, 41:5716-5723.
- Spain, Anne M., Aaron D. Peacock, Jonathan D. Istok, Mostafa S. Elshahed, Fares Z. Najjar, Bruce A. Roe, David C. White, and Lee R. Krumholz. 2007. Identification and Isolation of a *Castellaniella* Species Important during Biostimulation of an Acidic Nitrate- and Uranium-Contaminated Aquifer. *Applied and Environ. Micro.* 73:4892-4904.
- Zhang, F., G. T. Yeh, J. C. Parker, C. Wang, R. Gu, and P. M. Jardine. 2007. A reaction-based river/stream water quality model, Part II: Reaction network decomposition and model validation. *Journal of Hydrology*. (submitted).
- Zhang, F., G. T. Yeh, J. C. Parker, and P. M. Jardine. 2007. A reaction-based river/stream water quality model, Part I: Model development and numerical schemes. *Journal of Hydrology* (submitted).
- Zhang, F., L. Jiang, G. T. Yeh, and J. C. Parker. 2007. An Adaptive Local Grid Refinement and Peak/Valley Capture Algorithm to Solve Nonlinear Transport Problems with Moving Sharp-Fronts. *Transport in Porous Media Journal*. (in press).
- Amos, B.K., Y. Sung, K. E. Fletcher, T. J. Gentry, W.-M. Wu, C. S. Criddle, J. Zhou, and F. E. Löffler. 2007. Detection and quantification of *Geobacter lovleyi* strain SZ: implications for bioremediation at tetrachloroethene- (PCE-) and uranium-impacted sites. *Applied and Environmental Microbiology* (in press).
- Liu, J., Andrea K. Brown, Xiangli Meng, Donald M. Cropek, Jonathan D. Istok, David B. Watson, and Yi Lu. 2007. A catalytic beacon sensor for uranium with parts-per trillion sensitivity and million fold selectivity. *Proceedings National Academy of Sciences* 104(7):2056–2061.
- Luo, W., W.-M. Wu, T. Yan, C. S. Criddle, P. M. Jardine, J. Zhou, B. Gu. 2007. Influence of bicarbonate, sulfate, and electron donors on biological reduction of uranium and microbial community composition. *Applied Microbiology and Biotechnology*. (in press).
- Benjaporn Boonchayaanant, Peter Kitanidis, Craig Criddle. 2007. Growth and cometabolic reduction kinetics of a uranium- and sulfate- reducing *Desulfovibrio/Clostridia* mixed culture: Temperature effects. *Biotechnology and Bioengineering* (submitted).
- Kieft, TL, JK Fredrickson and TJ Phelps. 2007. Coring, drilling and sampling subsurface environments. MEM3 ASM Press. Chapter 66. Pp. 799-817.
- Madden, A.S., A.C. Smith, D. L. Balkwill and T. J. Phelps. 2007. Microbial uranium immobilization independent of nitrate reduction. *Environ. Microbiol.* 9:(9) 2321-2330.

- Phelps, TJ, AV Palumbo, BL Bischoff, CJ Miller, L. Fagan, MS McNeilly and R.R. Judkins. 2007. Micron-pore-sized metallic filter tube membranes for filtration of particulates and water purification *Journal of Microbiological Methods* (In press).
- Phelps, TJ and SM. Pfiffner. 2007. Tribute to the scientific contributions of David Cleveland White. *Journal of Microbiological Methods*. (In press).
- Madden, A.S., A V. Palumbo, B. Rave, T. A. Vishnivetskay, S. D. Kelly, C. Schad, T. J. Phelps, C. C. Brandt. 2007. Geochemical consequences of electron donor selection for bioremediation of uranium contaminated sediments. (submitted)
- Phillips, Debra H., Baohua H. Gu, David B. Watson, Charles S. Parmele. 2007. Uranium removal from contaminated groundwater by synthetic resins. *Water Research* (in press).
- Phillips, Debra H., David B. Watson, and Yul Roh. 2007. Uranium Deposition in a Weathered Fractured Saprolite/Shale. *Environ. Sci. Technol.* (in press).
- Ginder-Vogel, M., S.D. Kelly, Craig S. Criddle, Wei-min Wu, Jack Carley, Phillip Jardine, Kenneth M. Kemner, Scott Fendorf, 2007. "Micro-scale Heterogeneity in Biogeochemical Uranium Cycling", *American Institute of Physics Conference Proceedings*, 882, 190.
- Kelly, S.D., K.M. Kemner, J. Carley, C.S Criddle, P.M. Jardine, T.L. Marsh, D.H. Phillips, D.B. Watson, and W.M. Wu. 2007. Speciation of uranium in sediments before and after in situ bioreduction. *Environ. Sci. Technol.* (submitted).
- Kelly, S.D., B. Ravel, and K.M. Kemner. 2007. EXAFS and XRF spectra from FRC gravel. *Environ. Sci. Technol.* (in preparation).
- Spalding, B.P., and D. B. Watson. 2007. Passive sampling and analyses of common dissolved fixed gases in groundwater. *Environmental Science & Technology* (submitted).
- Cardenas, E., W. Wu, M. Leigh, J. Carley, S. Carroll, T. Gentry, J. Luo, D.B. Watson, B.H. Gu, M. Ginder-Vogel, P.K. Kitanidis, P.M. Jardine, Z. Zhou, C.S. Criddle, T.L. Marsh, and J.M. Tiedje. 2007. Microbial communities in contaminated sediments associated with bioremediation of uranium to submicromolar levels. *Applied Environ. Microbiology* (submitted).
- Luo, J., W.-M. Wu, J. Carley, H. Cheng, D. Watson, C.S. Criddle, P.M. Jardine, and P.K. Kitanidis. Estimating first-order reaction rate coefficients for transport with nonequilibrium linear mass transfer in heterogeneous media. *J. Contamin. Hydrol.* (submitted).
- Zhang, F., J. C. Parker, B. Gu, W. Luo, S. C. Brooks, P. M. Jardine and D. B. Watson. 2007. An ion exchange model for sorption of nickel, uranium and technetium onto amorphous aluminum hydroxide during titration of a contaminated groundwater. *Ground Water Journal*. (ready for submission).
- Zhang, F., B. Gu, J. C. Parker, W. Luo, B. P. Spalding, S. C. Brooks, D. B. Watson and P. M. Jardine. 2007. Geochemical reactions affecting aqueous-solid partitioning metals during titration of uranium contaminated soil. *Environmental Science & Technology*. (ready for submission).

Zhang, F., S. C. Brooks, J. C. Parker, Y.-J. Kim, P. M. Jardine, and D. B. Watson. 2007. Comparison of Approaches to Calibrate a Surface Complexation Model for U(VI) Sorption to Weathered Saprolite. *Transport in Porous Media Journal*. (ready for submission).

Kim, Y.-J., S. C. Brooks, W. Kamolpornwijit, F. Zhang, J. C. Parker, J.-W. Moon, and Y. Roh. 2007. Fate and Transport of Uranium (VI) in Weathered Saprolite. *Journal of Contaminant Hydrology*. (ready for submission).

Abstracts and Presentations

Zhang, F., J. C. Parker, B. Gu, W. Luo, S. C. Brooks, B. P. Spalding, P. M. Jardine, D. B. Watson. 2007. A geochemical reaction model for titration of contaminated soil and groundwater at the Oak Ridge Reservation. American Geophysical Union, December 10–14, 2007, San Francisco CA.

Kitianidis, P., J. Luo, W. Wu, J. Carley, T. Mehlhorn, D. Watson, C. Criddle, and P.M. Jardine. 2007. Hydraulic control for manipulating subsurface conditions for in situ experiments of U(VI) bioremediation. American Geophysical Union, December 10–14, 2007, San Francisco CA.

Long, P. et al. (with B.P Spalding). 2007. The Integrated Field-Scale Subsurface Research Challenge Site (IFC) at Rifle, Colorado: Preliminary Results on Microbiological, Geochemical and Hydrologic Processes Controlling Iron Reduction and Uranium Mobility. American Geophysical Union, December 10–14, 2007, San Francisco CA.

Van Nostrand, J. D., L. Wu, S. Carroll, Z. He, C. Criddle, P.M. Jardine, T. C. Hazen, and J. Z. Zhou. 2007. Changes in microbial community function during a period of reoxidation in a groundwater recirculation system. 15th Annual International Conference on Microbial Genomics, 16-20 Sept, College Park, MD.

Baker et al., 2007. Estimation of Site-Scale Temporal Variations in Seismic Response as a Function of Geophone Placement, American Geophysical Union, December 10–14, 2007, San Francisco CA.

Hubbard et al., 2007. Exploring Hydrological and Biogeochemical Processes associated with Remedial Treatments using Geophysical Methods, American Geophysical Union, December 10–14, 2007, San Francisco CA. (Invited).

H. Mills, J. E. Kostka, D. Akob, L. Kerkhof, K.-J. Chin. 2007. Cultivation independent quantification and characterization of metal and nitrate-reducing prokaryotes in radionuclide contaminated subsurface sediments. Annual Meeting of the American Society for Microbiology, Toronto, Canada, May 21-27, 2007..

Kostka, J.E. 2007. Metal reduction and metal-reducing microorganisms in the radionuclide-contaminated subsurface. Institute for Geosciences, Friedrich-Schiller University, Jena, Germany, July, 2007.

Wu, W.M., J. Carley, E. Cardenas, C. Hwang, S. D. Kelly, J. Van Nostrand, M. B. Leigh, B. Boonchayaanant, S. Carroll, K. Lowe, J. Luo, W. Luo, L. Wu, T. Mehlhorn, D. Watson, K. M. Kemner, M. W. Fields, B. Gu, J. Zhou, S. Fendorf, P. Kitanidis, T. L. Marsh, J. Tiedje, P. Jardine, C. S. Criddle. 2007. Biological Reduction/immobilization of Uranium to below EPA MCL levels in situ at the DOE ERSP Field Research Center, Oak Ridge, TN. American Society of Microbiology 107th General Meeting. Toronto, Canada. May 21-25, 2007.

Wu, L., T.J. Gentry, Z.J. Huang, C.W. Schadt, W.-M. Wu, D. Watson, Z. L. He, M. W. Fields, C.S.Criddle, J. Tiedje, T.C. Hanzen, J. Zhou. 2007. Microarray-based analysis of microbial community composition and dynamics in uranium bioremediation. Poster presented at American Society for Microbiology 107th General Meeting, Toronto, Canada. May 21-27, 2007.

Van Nostrand, Joy D., Yili Liang, Liyou Wu, Weimin Wu, Sue Carroll, Zhili He¹, Craig Criddle, Phil Jardine, Terry C. Hazen, and Jizhong Z. Zhou. 2007. Changes in Microbial Community Function During a Period of Reoxidation in a Groundwater Recirculation System. American Society for Microbiology 107th General Meeting, 20-24 May, Toronto, Canada.

Hwang, C., G.A. Corbin, W.-M.Wu, T.J. Gentry, J. Carley, S.L. Carroll, D. Watson, P.M. Jardine, J. Zhou, C.S. Criddle, and M.W. Fields. 2007. Changes in Microbial Community Structure During Biostimulation for Uranium Reduction. American Society for Microbiology 107th General Meeting, 20-24 May, Toronto, Canada.

Jardine, P.M. and D.B. Watson. 2007. Exploring subsurface bioreduction and immobilization of U and co-contaminants at the Oak Ridge Field Research Center: Past, current, and future research endeavors. 2007 Environmental and Subsurface Science Symposium, featuring Biotechnology and Bioremediation. Logan Utah, July 25-27.

Watson, D.B., and P.M. Jardine. 2007. An Overview of Research Activities and Findings from the DOE Environmental Remediation Sciences Program, Oak Ridge Field Research Center. Global Uranium Symposium. The South Texas Mineral Section of the SME. Corpus Christi, Texas. May 21-24, 2007.

Leigh, Mary Beth, Erick Cardenas, Wei-Min Wu, Ondrej Uhlik, Jack Carley, Sue Carroll, Terry Gentry, Terence L. Marsh, Jizhong Zhou, Philip Jardine, Craig S. Criddle and James M. Tiedje. 2007. Microbial bioremediation of a uranium(VI) contaminated aquifer. 4th Symposium on Biosorption and Bioremediation. Prague, Czech Republic, August 26th - 30th, 2007.

Jardine, P.M. and D.B. Watson. 2007. Overview of the ERSD project “Multi-scale Investigations on the Rates and Mechanisms of Targeted Immobilization and Natural Attenuation of Metal, Radionuclide and Co-Contaminants in the Subsurface” National Academy of Sciences. Oak Ridge National Laboratory, June 14-15, 2007.

Kemner, K.M., E. J. O’Loughlin, S. D. Kelly, B. Ravel, M. Boyanov. Investigations of coupled biogeochemical processes affecting the transformation of U: Integration of synchrotron-based approaches. Environmental Remediation Science Program Annual PI Meeting, Landsdowne, VA, April 16-19, 2007.

Jardine, P.M. and D.B. Watson. 2007. Exploring subsurface bioreduction and immobilization of U and co-contaminants at the Oak Ridge Field Research Center: Past, current, and future research endeavors. 2007 Environmental and Subsurface Science Symposium, featuring Biotechnology and Bioremediation. Logan Utah, July 25-27.

Matthew Ginder-Vogel, S.D. Kelly, Craig S. Criddle, Wei-min Wu, Jack Carley, Phillip Jardine, Kenneth M. Kemner, Scott Fendorf, “Micro-scale Heterogeneity in Biogeochemical Uranium Cycling”, 13th International Conference on X-ray Absorption Fine Structure, Program and Abstracts, Stanford, California, July 9-14, 2006.

Response to Reviewer Comments on Proposal

The ORIFC proposal was reviewed by more than 15 individuals prior to a decision of funding. Reviewer comments of concern were complied by ERSD staff, passed along to the project PI, and each comment was addressed in detail by the project research team and returned to ERSD staff. Most comments required only clarification of the proposed tasks. Other comments were incorporated into a revised research plan, while other comments, although constructive, could not be accommodated because of financial constraints. There were no comments of significance that disputed the scientific integrity of the proposed hypotheses or the research tasks

that were proposed to test these hypotheses. Reviewer comments and responses are available upon request. Summarized comments are presented below.

Microbiological Issues

General reviewer comments: The reviewer comments can be considered in two categories: 1) issues related to standardization and calibration of molecular techniques, and 2) sampling issues.

The comments were addressed in detail by the various PIs of the project and the proposed research was clarified but not altered by the comments.

Modeling Issues

Reviewers Comment: What will be learned about multi-scale behavior, methods to scale behavior and methods to extract rate controlling coupled process(es) from the experiment design is unclear. Emphasis is on development of a tool. The multiscale model really does not present a plan well connected to hypotheses.

Reviewer Comment: While the need for upscaling is acknowledged, no methodology is described except for “Numerical analyses ... to integrate results from across scales ... “. The suggested variance-based based scaling may be a very daunting numerical task for a complex HYDROGEOCHEM model with many parameters.

The comments were addressed in detail by the various PIs of the project and the proposed research was clarified but not altered by the comments.

Hydrology and Geochemistry Issues

Reviewers comment: Given the importance of hydrogeologic experiment design, it would be nice to see greater hydrogeologic expertise on the team. In addition, the multi-scale aspects do not appear to be well supported by the modeling team.

Reviewers comment: The surface analytical section is a weak component of the proposed study, but will ultimately be critical in the development of an accurate conceptual model for the HYDROGEOCHEM simulations, especially if surface complexation models are to be used.

Reviewers comment: The design of the overall research program and individual project is very well done, and because of that I was surprised to not find a clear extension of this research program to the groundwater/surface water interface where significant geochemical gradients occur and where significant contaminant transformation and geochemical shifts would be expected. The emphasis on multiscale investigations from molecular to watershed seem to ignore this very dynamic groundwater/surface water interface, and as mentioned briefly below, this seem a lost opportunity to explore the overall research questions posed in the proposal regarding coupled hydrologic, geochemical and microbiological processes affecting contaminant fate and transport in a very interesting and dynamic portion of watersheds, the groundwater/surface water interface, that would be relevant to many contaminated sites in the DOE system.

The comments were addressed in detail by the various PIs of the project and the proposed research was altered to a limited extent due to a finite financial budget. The PIs consider groundwater – surface water issues extremely important at the watershed scale, however, experimental and numerical advances in this area will require a significant increase in funds.

Geophysical Issues

Reviewers comment: The team should be much clearer about why they wish to carry out particular

measurements – as it stands the approach appears to be high risk (e.g. “if reliable petrophysical relationships can be developed” (page 1-17)). Surely the team should decide what specific hydrochemical information they require and adopt an appropriate methodology to address this? The team aim to use time-lapse seismic and resistivity methods for monitoring recharge. The purpose of seismic methods for this study is not clear to me – are structural changes expected, say at precipitation fronts? Is it realistic to expect to be able to see such changes? I was also disappointed that there is no direct reference to the use of geophysics to bridge scales. In my view this is the real value of geophysics for a proposal such as this. I suspect that the geophysical experiments will run in a degree of isolation from the other tasks and this would be a great shame. One of the key challenges has to be how we use detailed knowledge at a small scale to inform at a larger scale. The proposal offers little insight into how this will be done.

Reviewers comments: I feel that the project team possibly lacks the strength in geophysics and rock physics that is needed to conduct this level of geophysical acquisition, analysis, and data integration.

The comments were addressed in detail by the various PIs of the project and the proposed research was clarified but not altered by the comments.